

**Ruthenium phthalocyanine
complexes: synthesis,
properties and applications.**

by

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A thesis submitted for the
degree of Doctor of Philosophy (Science)

University of Technology, Sydney

2008

Certificate of authorship and originality

I certify that the work in this thesis has not previously been submitted for a degree nor has it been submitted as part of the requirements for a degree except as fully acknowledged within the text.

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DATE 17/6/2009

In memory of:

Rudolf Rathbauer

22.01.1926 - 06.09.2005

Helga Gertrude Rathbauer

25.01.1929 - 10.08.2008

Acknowledgements

First and foremost, I would like to thank my supervisor Andrew McDonagh. You provided me not only a very successful project and a scholarship, but also unlimited time, guidance, knowledge and patience (particularly in my first year). I have learnt so much working with you, most importantly a genuine curiosity in chemistry and an ability to conduct high quality research. The skills and knowledge you have instilled in me fill me with confidence and I am extremely grateful.

I guess I should thank the b*stard men; Mark Tahtouh and Ron Shimmon. Ronald, you have given so generously of your time and I have learnt a lot from you. You have taught me everything from practical synthetic chemistry to treating the NMR spectrometer like a woman. I am very grateful. Mark, I feel I must thank you to be polite.

I must also thank the many people I have collaborated with during the course of my project. Thanks to Steve Colbran for your help with the electrochemistry, and your patience in going through some fairly “crude” manuscripts. Thanks also to Hadi Zareie for collecting the STM images shown in Chapter 6. I would like to thank to Christine Austin and Dominic Hare for your work on the ICP-MS; even if you did just press the start button. I would also like to thank Sang-Tae Lee for teaching me how to use the electrochemistry instrumentation and Florian Buchholz for assistance in the DSC work. I must also mention Jim Keegan and Nigel Lucas for their help.

I have shared an office with a lot of great people and your company (at times) has made my time at UTS very enjoyable. So thanks, in chronological order to; Al Beavis, Mat Foot (of the Foot-Kirkup equation), Sonia Taflaga, Bec Webb, Mark Tahtouh, Katherine Bojko, Lisa Mingari, Kate Grimwood, Ellen Braybon, Dominic Hare, Christine Austin, Jess Booth (yes, even you) and Thesis Write-up Fish.

Last but not least I would like to thank my family and friends. Thanks to my beautiful partner Steph for her love and patience. I look forward to actually earning money so we can start a life together. Also thanks to mum and dad. I would not be where I am without you.

Table of contents

Certificate of authorship and originality	ii
Acknowledgements	iv
Table of contents	v
List of figures	ix
List of tables	xiv
Abbreviations	xv
Publications arising from this work	xx
Abstract	xxi
Chapter 1: Ruthenium Phthalocyanine and Naphthalocyanine Complexes	2
1.1 Introduction	2
1.2 Synthesis	3
1.2.1 Synthesis of complexes with unsubstituted phthalocyanine macrocycles	3
1.2.2 Synthesis of complexes with substituted phthalocyanine macrocycles	12
1.2.3 Synthesis of naphthalocyanine complexes	23
1.3 Properties of ruthenium phthalocyanine and naphthalocyanine complexes	25
1.3.1 Spectroscopic properties	25
1.3.2 Redox chemistry	33
1.3.3 Conduction properties of polymers	39
1.4 Applications	43
1.4.1 PcRu as thin films	43
1.4.2 Catalysis	47
1.4.3 Photodynamic therapy	51
1.4.4 Dye-sensitised Solar Cells	53
1.5 Conclusions	55

Chapter 2: Optical and Redox Properties of Ruthenium Phthalocyanine Complexes Tuned with Axial Ligand Substituents.	58
2.1 Introduction	58
2.2 Experimental	60
2.2.1 General.....	60
2.2.2 Synthesis	62
2.3 Results and Discussion	64
2.3.1 Synthesis.	64
2.3.2 ¹ H NMR spectroscopy.	65
2.3.3 Electrochemistry.	67
2.3.4 UV-visible spectroscopy.	70
2.3.5 Spectroelectrochemistry.....	72
2.4 Conclusions	77
Chapter 3: Synthesis, Electrochemistry and Spectroscopic Properties of Ruthenium Phthalocyanine and Naphthalocyanine Complexes with Triphenylarsine Ligands.	79
3.1 Introduction	79
3.2 Experimental	81
3.2.1 General.....	81
3.2.2 Synthesis	82
3.3 Results and Discussion	84
3.3.1 Synthesis	84
3.3.2 ¹ H NMR spectroscopy	85
3.3.3 Electrochemistry	88
3.3.4 UV-visible spectroscopy	90
3.4 Conclusions	93

Chapter 4: Ruthenium Phthalocyanine – Bipyridyl Dyads as Sensitisers for Dye-Sensitised Solar Cells.....	95
4.1 Introduction	95
4.2 Experimental	100
4.2.1 General.....	100
4.2.2 Synthesis.	101
4.2.3 DSC fabrication and characterisation.....	108
4.2.4 Dye Coverage Measurements.....	110
4.3 Results and Discussion	110
4.3.1 Synthesis	110
4.3.2 ^1H NMR spectroscopy.	117
4.3.3 UV-vis spectroscopy.....	123
4.3.4 Electrochemistry	125
4.3.5 Spectroelectrochemistry.....	131
4.3.6 TiO_2 Surface Adsorption.....	136
4.3.7 Photovoltaic performance.	138
4.4 Conclusions	141
Chapter 5: Convenient Synthesis and Purification of $[\text{Bu}_4\text{N}]_2[\text{Ru}(4\text{-carboxy-4-carboxylate-2,2'-bipyridine})_2(\text{NCS})_2]$: A Landmark DSC Dye.	144
5.1 Introduction	144
5.2 Experimental	145
5.2.1 General.....	145
5.2.2 Synthesis	146
5.3 Results and Discussion	148
5.3.1 Synthesis	148
5.3.2 ^1H NMR spectroscopy	150

5.4	Conclusion.....	151
Chapter 6:	Thin Films of Ruthenium Phthalocyanine Complexes on Gold Surfaces.	153
6.1	Introduction	153
6.2	Experimental.....	155
6.2.1	General.....	155
6.2.2	Synthesis.	156
6.2.3	Gold Substrates.....	158
6.2.4	Assembly	158
6.2.5	Scanning Tunneling Microscopy	158
6.2.6	LA ICP-MS.....	159
6.2.7	Solution ICP-MS.....	159
6.3	Results and discussion	160
6.3.1	Synthesis	160
6.3.2	^1H NMR spectroscopy.	162
6.3.3	UV-vis spectroscopy.....	163
6.3.4	Thin film surface density.....	164
6.3.5	LA ICP-MS analysis of thin films	168
6.4	Conclusion.....	173
Chapter 7:	General Conclusions.....	175
7.1	General discussion and conclusions.....	175
7.2	Future directions.....	177
Appendix	179
References	181

List of figures

Figure 1. Left: Ruthenium phthalocyanine (PcRu). Right: Ruthenium 2,3-naphthalocyanine (2,3-NcRu).	2
Figure 2. The [PcRu(pyz)] _n polymer reported by Hanack et al. ⁶⁴	11
Figure 3. Numbering scheme for Pc ring positions.	12
Figure 4. Positional isomers of tetra-substituted ruthenium phthalocyanine.	13
Figure 5. [2,3-NcRu] (left), and [{(t-Bu) ₄ -2,3-Nc}Ru] (right, only one isomer shown).....	23
Figure 6. UV-visible spectrum of [{2,9,16,23-(t-Bu) ₄ Pc}Ru(4-Mepy) ₂] in dichloromethane.	25
Figure 7. Diagram showing designation of α and β protons in PcRu.	30
Figure 8. The water soluble complex K ₂ [PcRu(TPPMS) ₂].	52
Figure 9. Schematic diagram of a DSC.	53
Figure 10. Complexes [{(t-Bu) ₄ Pc}Ru(4-Rpy) ₂] described in this chapter.....	58
Figure 11. Cyclic voltammograms of 1 – 4 in dichloromethane solution with 0.1 M [Bu ₄ N][PF ₆] electrolyte. Scan rate: 100 mV s ⁻¹	67
Figure 12. Graph showing oxidation potentials (E _{1/2} /V vs. Fc ⁺ /Fc) of 1 – 4 vs. pK _a of the axial ligands, 4-Rpy (● = NO ₂ , ▲ = Me, ◆ = NH ₂ , ■ = NMe ₂). (a) First oxidation. (b) Second oxidation.	69
Figure 13. UV-visible spectra of 3 (solid line) and 4 (dashed line) in dichloromethane.	70
Figure 14. UV-visible spectra recorded during the first oxidation of 1 (at 0.39 V vs. Fc ⁺ /Fc) in dichloromethane / 0.1 M [n-Bu ₄ N][PF ₆]. Isosbestic points at 691, 568, 418, 371, 337, 306 and 254 nm.	72
Figure 15. UV-visible spectra recorded during the second oxidation of 1 at up to +1.1 V vs. Fc ⁺ /Fc in dichloromethane (0.1 M [n-Bu ₄ N][PF ₆]).	73

Figure 16. UV-Visible spectra recorded during the second oxidation of 3 at up to + 0.6 V vs. Fc/Fc ⁺ in dichloromethane (0.1 M [n-Bu ₄ N][PF ₆]).....	74
Figure 17. UV-visible spectra recorded during the first reduction of 3 at up to -2.2 V vs. Fc ⁺ / Fc in dichloromethane (0.2 M [n-Bu ₄ N][PF ₆]).....	75
Figure 18. UV-Visible spectra of 2 (solid line) and the electrochemically generated 4 ²⁻ (dashed line) in dichloromethane.....	76
Figure 19. UV-visible spectra of 4 ³⁻ (dashed line) and 2 ⁻ (solid line) in dichloromethane.	77
Figure 20. [PcRu(AsPh ₃) ₂] (7) and [{(t-Bu) ₄ -2,3-Nc}Ru(AsPh ₃) ₂] (8) (only one positional isomer shown).....	79
Figure 21. ¹ H NMR spectrum of 7 (0.8 mM) in CDCl ₃	86
Figure 22. Cyclic voltammograms of 7, 8 and AsPh ₃ in dichloromethane solution with 0.1 M [n-Bu ₄ N][PF ₆] electrolyte. Scan rate: 100 mV s ⁻¹	88
Figure 23. UV-Visible spectrum of 7 (solid line) and 8 (dashed line) in degassed dichloromethane.....	90
Figure 24. UV-Visible spectra of 7 in dichloromethane recorded over 7 hour upon exposure to air.	91
Figure 25. UV-Visible spectra of 8 in dichloromethane recorded over 7 hour after exposure to air.	91
Figure 26. Dyads 23a and 23b that incorporate bis(bipyridyl)ruthenium(II) and ruthenium phthalocyanine chromophores.....	95
Figure 27. A schematic representation of the operation of a DSC.	96
Figure 28. Direct solar flux (US Standard Atmosphere; AM = 1.5).....	97
Figure 29. Electron transfer processes in acceptor-sensitiser (left) and sensitiser-donor (right) complexes anchored on TiO ₂	99

Figure 30. The four stereoisomers of 19, 20 and 21. The dashed line shows the mirror plane between the enantiomers.	115
Figure 31. The ^1H NMR spectrum of 19 in CDCl_3	117
Figure 32. 3-Dimensional representation of 19 showing the pyridyl protons in close proximity to the chloro ligands (interaction indicated with a double-headed arrow).	118
Figure 33. The ^1H NMR spectrum of 22b in CDCl_3 with peak assignments.....	119
Figure 34. ^1H - ^1H COSY NMR spectrum of 22b showing only the aromatic region.	119
Figure 35. The ^1H NMR spectrum of 22a in CDCl_3 with peak assignments.....	121
Figure 36. ^1H - ^1H COSY NMR spectrum of 22a showing only the aromatic region.....	121
Figure 37. UV-visible spectra of 18 (dotted line), 20 (dashed line) and 22a (solid line) in dichloromethane.....	123
Figure 38. Cyclic voltammograms of the ruthenium phthalocyanine complexes 15 - 18 in dichloromethane solution with 0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ electrolyte. Scan rate = 100 mV s^{-1}	126
Figure 39. Cyclic voltammogram of 16 in which the forward sweep is stopped just beyond the second oxidation. Conditions: dichloromethane with 0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ electrolyte; glassy carbon minidisk (0.5 mm) working electrode, scan rate = 100 mVs^{-1}	127
Figure 40. Cyclic voltammogram of 21 in dichloromethane solution with 0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ electrolyte; glassy carbon minidisk (0.5 mm) working electrode, scan rate = 100 mV s^{-1}	128
Figure 41. Cyclic voltammograms of 23a and 23b in dichloromethane solution with 0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ electrolyte; glassy carbon minidisk (0.5 mm) working electrode, scan rate = 100 mV s^{-1}	129
Figure 42. UV-Vis spectra recorded during the oxidative electrolyses of 18 in dichloromethane (0.1 M $[\text{n-Bu}_4\text{N}][\text{PF}_6]$). (a) first oxidation process at 0.15 V. (b) second oxidation process at 0.82 V.	131

Figure 43. UV-Vis spectra recorded during the reductive electrolyses in dichloromethane (0.2 M [n-Bu ₄ N][PF ₆]). (a) initial reduction of 18 at -1.95 V. (b) reduction of 17 at -2.00 V after initial changes were complete.	132
Figure 44. UV-Vis spectra recorded during the reduction (a) and first oxidation (b) of 21 in dichloromethane/DMF (0.1 M/0.2 [n-Bu ₄ N][PF ₆] for the oxidation/reduction) using a Pt electrode.	134
Figure 45. UV-Vis spectra recorded during the oxidative electrolyses of 23b in dichloromethane (0.1 M [n-Bu ₄ N][PF ₆]): (a) first oxidation process at 0.26 V: (b) second reduction process at -1.95 V.	135
Figure 46. Typical illuminated and dark J – V curves of DSCs prepared with the sensitising dyes anchored on TiO ₂ films. Dark J – V curves start at 0 mA cm ⁻²	138
Figure 47. The sensitising dye cis-[Ru(H ₂ dcbpy) ₂ (NCS) ₂].	144
Figure 48. Aromatic region of the ¹ H NMR spectrum of the isothiocyanate complex N719 showing an isomerically pure product (solvent: methanol-d ₄).	151
Figure 49. Ruthenium phthalocyanine complexes investigated in this chapter.	154
Figure 50. UV-visible spectra of 28 (solid line), 31 (dashed line) and 32 (dotted line) in dichloromethane solution.	163
Figure 51. Dimensions (hydrogen to hydrogen) obtained by molecular modeling of ruthenium phthalocyanine and ruthenium tetra-tert-butyl phthalocyanine rings. Axial ligands are omitted for clarity.	164
Figure 52. STM images of 27 thin film on Au(111).	166
Figure 53. STM image (58 x 58 nm) of a thin film of 31 on Au(111).	166
Figure 54. STM images of a thin film of 30 on Au(111).	167
Figure 55. The vaporisation of ruthenium phthalocyanine molecules and underlying gold during the ablation process.	168

Figure 56. LA ICP-MS signals of ^{101}Ru generated from line scans of gold substrates coated with thin films of 30 after 12 hours immersion (a), and 28 after 6 hours immersion (b)..... 169

Figure 57. Intensity ratio vs time plot for ^{101}Ru isotope of 28 film. Inset is a closer view of the trend observed before 1 hour. 172

List of tables

Table 1. Electrochemical potentials, V vs Fc^+/Fc for selected PcRu complexes.	34
Table 2. Conductivity data for pressed polymer powders.	40
Table 3. ^1H NMR Chemical Shifts for 1-4 in CDCl_3	65
Table 4. Electrochemical Data from Cyclic Voltammetry Experiments ^a	68
Table 5. Electronic absorption maxima and molar absorptivities ^a of $[(\text{t-Bu})_4\text{Pc}\text{Ru}(4\text{-Rpy})_2]$ complexes.	71
Table 6 Electrochemical data. ^{a,b}	125
Table 7. Photovoltaic Performance Data for DSCs prepared with the sensitising complexes investigated in this work. ^{a,b}	139
Table 8. ICP-MS data for thin films of 27 – 31. ^a Repeat measurements not performed.	165
Table 9. Intensity ratios recorded for thin films of complexes 27 – 31 on gold using LA ICP-MS.	170

Abbreviations

3-atri = 3-amino-1,2,4-triazine

3-Clpy = 3-chloropyridine

3-Fpy = 3-fluoropyridine

3,4-py(COOAc)₂ = bis(2-oxopropyl)pyridine-3,4-dicarboxylate

4-pyCH₂SAc = S-(pyridine-4-ylmethyl)ethanthioate

4-pyCOOAc = (2-oxopropyl)pyridine-4-carboxylate

5-atri = 5-amino-1,2,4-triazine

Ace = acetyl

apy = 4-aminopyridine

bpy = 4,4'-bipyridine

bpyac = 4,4'-bipyridylacetylene

Bpy = butylpyridine

t-Bu₂dib = 2,5-di-*t*-butyl-1,4-diisocyanobenzene

t-Bupyz = 2-*t*-butylpyrazine

(C₈H₁₇)₂dib = 2,5-dioctyl-1,4-diisocyanobenzene

(C₁₀H₂₁)₂dib = 2,5-didecyl-1,4-diisocyanobenzene

(CN)₂C₆F₄ = 2,3,5,6-tetrafluoro-1,4-dicyanobenzene

Cl₂tz = 3,6-dichloro-s-tetrazine

Cl₄dib = 2,3,5,6-tetrachloro-1,4-diisocyanobenzene

Clpyz = 2-chloropyrazine

dabco = 1,4-diazabicyclo[2.2.2]octane

daf = 2,7-diaminofluorene

datz = diamin-s-otetrazine

DBU = 1,8-diazabicyclo[5,4,0]unde-7-cene

dcbpy = 2,2'-bipyridine-4,4'-dicarboxylic acid

dia = 9,10-diisocyananthracene

dib = 1,4-diisocyanobenzene

DMF = dimethylformamide

DMSO = dimethyl sulfoxide

DSC = Dye-sensitised Solar Cell

Etpyz = 2-ethylpyrazine

Fc = ferrocene

F₄dib = 2,3,5,6-tetrafluoro-1,4-diisocyanobenzene

H₂dcbpy = 4,4'-dicarboxylic acid-2,2'-bipyridine

HOMO = Highest Occupied Molecular Orbital

*i*Bu₂dcbpy = bis(2-methylpropyl)-2,2'-bipyridine-4,4'-dicarboxylate

ICP-MS = Inductively Coupled Plasma-Mass Spectrometry

im = imidazole

iqnl = isoquinoline

*J*_{sc} = short circuit current density

LA ICP-MS = Laser Ablation Inductively Coupled Plasma-Mass Spectrometry

LUMO = Lowest Unoccupied Molecular Orbital

lut = lutidine

Medib = 2-methyl-1,4-diisocyanobenzene

Me₂dcbpy = dimethyl-2,2'-bipyridine-4,4'-dicarboxylate

Me₂dib = 2,5-dimethyl-1,4-diisocyanobenzene

Me₄dib = 2,3,5,6-tetramethyl-1,4-diisocyanobenzene

Meim = *N*-methylimidazole

Mepy = methylpyridine

Me₂pyNC = 4-isocyano-3,5-dimethylpyridine

Mepyz = 2-methylpyrazine

Me₂pyz = 2,6-dimethylpyrazine

Me₂pyz = 2,6-dimethylpyrazine

Meqnx = 2-methylquinoxaline

Me₂tz = 3,6-dimethyl-s-tetrazine

N3 = *cis*-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato)-ruthenium(II)

N719 = *cis*-bis(isothiocyanato)bis(4-carboxy-4-carboxylate-2,2'-bipyridine)-ruthenium(II) bis-tetrabutylammonium

Nc = naphthalocyanine

npd = 1,5-naphthyridine

Pc = phthalocyanine

pdz = pyridazine

PhCN = benzonitrile

PhNC = isocyanobenzene

P_{max} = maximum power output

PMMA = poly(methyl methacrylate)

Pn = porphyrin

ppd = *p*-phenylenediamine

ptz = phthalazine

py = pyridine

pypyz = pyrido[2,3-*b*]pyrazine

pyz = pyrazine

qnl = quinoline

qnz = quinazoline

qnx = quinoxaline

RSD = Relative Standard Deviation

SAM = Self-Assembled Monolayer

SOMO = Singly Occupied Molecular Orbital

STM = Scanning Tunneling Microscope

TBA = tetra-*n*-butylammonium

TBAOH = tetra-*n*-butylammonium hydroxide

t-Bu = *tert*-butyl

thf = tetrahydrofuran

tri = 1,2,4-triazine

triest = 3-Ethoxycarbonyl-1,2,4-triazine

TPP = tetraphenylporphyrin

tz = *s*-tetrazine

V_{oc} = open circuit voltage

Publications arising from this work

1. Rawling, T. and A. McDonagh (2007). "Ruthenium phthalocyanine and naphthalocyanine complexes: Synthesis, properties and applications." *Coordination Chemistry Reviews* **251**: 1128-1157.
2. Rawling, T., Xiao, H., Lee S.-T., Colbran S. B., McDonagh A. M. (2007). "Optical and Redox Properties of Ruthenium Phthalocyanine Complexes Tuned with Axial Ligand Substituents." *Inorganic Chemistry* **46**(7): 2805-2813.
3. Rawling, T., A. M. McDonagh, S.B. Colbran. (2008). "Synthesis, electrochemistry and spectroscopic properties of ruthenium phthalocyanine and naphthalocyanine complexes with triphenylarsine ligands." *Inorganica Chimica Acta* **361**(1): 49-55.
4. Rawling, T., F. Buchholz, A.M. McDonagh. (2008). "Convenient Synthesis and Purification of $[\text{Bu}_4\text{N}]_2[\text{Ru}(\text{4-carboxy-4-carboxylate-2,2'-bipyridine})_2(\text{NCS})_2]$: a Landmark DSC Dye." *Australian Journal of Chemistry* **61**(6): 405-408.

Abstract

Ruthenium phthalocyanine and naphthalocyanine complexes are an extremely useful and adaptable class of inorganic complex that have been the focus of a large body of research. They are very stable and may be readily synthesised by a variety of routes. They are able to coordinate a large variety of functionalised ligands, and possess tuneable UV-vis absorbance and electrochemical processes, all of which makes them suitable for a wide variety of applications. Polypyridyl complexes of ruthenium, considered in the latter part of this thesis, also exhibit useful electronic and electrochemical properties that make them appropriate for many applications, particularly in the area of photovoltaic devices. In this thesis the syntheses of thirty new ruthenium phthalocyanine, ruthenium naphthalocyanine and ruthenium polypyridyl complexes are presented, and the properties and applications of these complexes are explored.

Chapter 1 of this thesis reviews the synthesis, properties, and applications of previously reported ruthenium phthalocyanine and naphthalocyanine complexes. The synthesis section examines ring forming syntheses, incorporation of ruthenium into the phthalocyanine macrocycle, and axial ligand exchange reactions. The spectral properties (^1H NMR, UV-vis and infra-red) of ruthenium phthalocyanines are examined, as well as redox and conductivity properties. The application of ruthenium phthalocyanine complexes as thin films and catalysts is explored, together with their use as sensitising dyes in photodynamic therapy and photovoltaic devices.

In Chapter 2 the optical and electrochemical properties of ruthenium phthalocyanine complexes bearing substituted pyridine axial ligands with varying electron withdrawing and donating abilities are discussed. The electron density at the phthalocyanine macrocycle may be adjusted using the axial ligands. Electrochemical data show that the axial pyridine ligands exert significant influence over the phthalocyanine ring-based redox processes. The axial ligands also influence the electronic absorption properties of the complexes with the influence also observed in the electrogenerated oxidised and reduced species.

Chapter 3 explores the synthesis, electrochemistry and spectroscopic properties of the first examples of metal phthalocyanine and naphthalocyanine complexes with axially-coordinated arsine ligands. The AsPh_3 ligands readily dissociate in non-coordinating solvents with the

naphthalocyanine showing more rapid dissociation than the phthalocyanine analog. In cyclic voltammetry experiments, the phthalocyanine analog displayed three macrocycle-centred redox processes; one reduction and two oxidation processes. One reduction and three oxidation processes were observed for naphthalocyanine analog. The reduction and first oxidation are assigned to macrocycle-centred processes. The UV-vis spectra of both complexes recorded over time showed macrocycle-centred oxidation. The rate of oxidation was slowed by removing dioxygen from the solvent or adding excess AsPh_3 .

In Chapter 4 the application of ruthenium phthalocyanine complexes as sensitising dyes in Dye-sensitised Solar Cells (DSCs) is explored. Solar energy conversion is emerging as an important area of research and DSCs offer a promising low cost alternative to conventional silicon-based solar cells. In addition to low cost, these cells may be flexible and semi-transparent and therefore incorporated into building materials and other devices. A major hurdle to widespread use of DSCs is efficiency, with the best DSCs operating at approximately half the efficiency of silicon-based solar cells. Four monomeric ruthenium phthalocyanine complexes are reported that vary in peripheral substitution and axial ligand anchoring groups. Sensitising dyes that contain two ruthenium centres are also presented. These dyads, which contain phthalocyanine and bipyridyl chromophores, were prepared using a protection/deprotection strategy that allows for convenient purification. DSCs fabricated using the phthalocyanine complexes and dyads were less efficient than those incorporating a standard DSC dye. However, based on the number of molecules bound to the TiO_2 electrode surfaces, several of the new complexes were more efficient at photocurrent generation. The results highlight the importance of molecular size, and thus the dye coverage of the electrode surface in the design of new sensitising dyes

Literature procedures that describe syntheses of the landmark DSC dye $[\text{Bu}_4\text{N}]_2[\text{Ru}(4\text{-carboxy-4-carboxylate-2,2'-bipyridine})_2(\text{NCS})_2]$ (N719) either yield an impure product or are highly time consuming. In Chapter 5 a convenient synthesis of N719 is presented. Key to this synthetic procedure is the protection of the carboxyl functionalities with *iso*-butyl ester groups. This strategy allows the use of silica chromatography to remove the less efficient S-bound isomers and significantly reduces the time and difficulty of the synthesis.

Chapter 6 investigates the absorption of ruthenium phthalocyanine complexes bearing functionalised axial ligands on gold surfaces. The surface chemistry of ruthenium phthalocyanines is fundamental to several topics explored in this thesis, and gold provides a

smooth surface on which to conduct experiments. The chapter also introduces the novel application of Laser Ablation Inductively Coupled Plasma Mass Spectroscopy (LA ICP-MS) to the analysis of metal containing thin films. It was found that the peripheral substituents on the phthalocyanine ring affect the surface density of thin films. It was also discovered that thin films reach a maximum density after only one minute of immersion of the gold substrate in a solution of the complex.

The final chapter of this thesis, Chapter 7, summarises the work presented in this thesis and highlights the key findings. It also outlines some directions for further possible research continuing from the work presented.